

**Fate of electrogenerated species
(radical-anion, dianon and/or
anion) at a platinum cathode at
very negative potentials
($E < -2.5$ V. vs SCE)**

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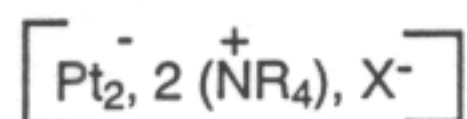
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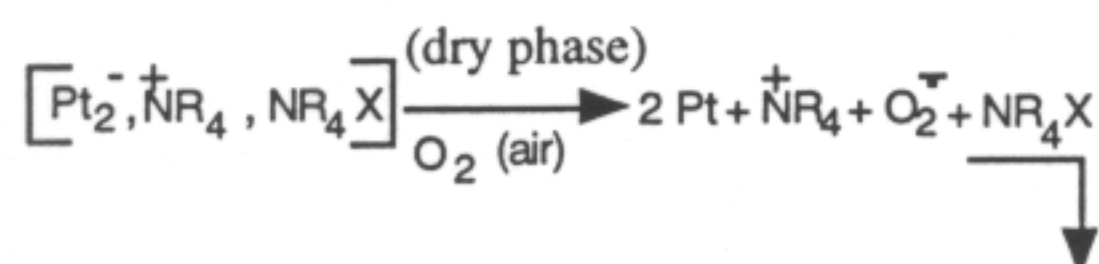
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The modification of platinum and palladium electrodes at rather negative potentials in aprotic solvents like dimethylformamide in the presence of

tetraalkylammonium NR_4^+ halides, perchlorate, tetrafluoroborate etc... has been very recently demonstrated. This cathodic modification occurs in mass of the electrode and in the presence of halide anions X^- ; with platinum, the nature of the cathodically produced phase has generally the following stoichiometry :



This phase can be electrochemically and chemically (for example by dioxygen) oxidized and lead to the emerging of the electrolyte from the metal.

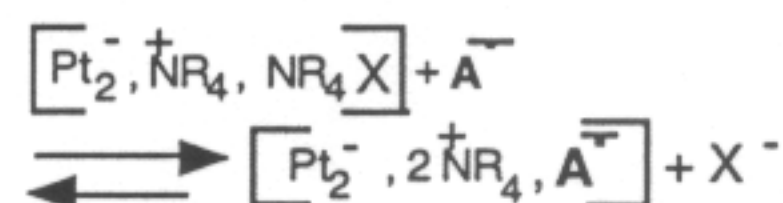


Such platinum complexes were shown to be rather efficient reducing reagents toward organic species (like aromatic ketones or aromatic hydrocarbons whose colored anion radicals immediately appear once in the contact with the interface Pt/dry solvent).

After a fine characterization of the nature of the change within a platinum layer whose thickness depends on the amount of electricity injected (say between a few nanometers to several micrometers), new questions arise :

(i) Could we achieve the reduction of an acceptor A (taken here as model for electroactive species) at the interface by means of the complex used here as interfacial mediator ?

(ii) Do we have an exchange between A^- and X^- and then get a new organometallic species encapsulating A^- such as :



(iii) Is the dianon A^{2-} (formed via disproportionation or by reduction at very negative potential) capable to be incorporated within the complex ?

Moreover, is A^- able to reduce the platinum interface to afford the interfacial formation of a complex which would catch highly stable acceptor reduced species ?

In this communication, preliminary experiments are presented with compounds giving stable anion radicals and dianons or anions (by cathodic cleavage). Thus, the compounds such as 1,4-diacetylbenzene, anthraquinone, acenaphthenequinone and phenanthrenequinone, were studied using cyclic voltammetry (CV) and electrochemical quartz microbalance (EQCM) technique.

REFERENCES :

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